OPTICAL PROPERTIES OF CLOSE-PACKED AND SPARSE QUANTUM DOT ARRAYS

by

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ABSTRACT

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We studied the shift that occurs in the electronic states of quantum dot arrays as dot spacing is varied. CdSe nanocrystals were synthesized and put into films with optical quality sufficient for absorption and electroabsorption experiments. Chemical procedures were used to make and stabilize the nanocrystals, and several different methods of CdSe synthesis were explored. Electrodes were used to put an electric field across the CdSe samples during the electroabsorption experiments. These were made by etching an electrode pattern into chromium covered sapphire disks using photolithographic procedures. The spacing between CdSe nanocrystals was varied using the polymer PMMA, and the absorption results suggested that the CdSe arrays progressed from a smooth spread of electron energy transitions to sharp electron energy transitions as the nanocrystal spacing increased.

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Chapter 1

Overview

Quantum effects and properties are generally associated with interactions that occur in small particles. For example, electron energy levels are discrete for atoms and molecules. Of noteworthy importance, however, are the electronic properties of particles that range approximately in size from 1-10 nm. Solid structures of this type have become known as quantum dots. These nanocrystalline structures are large enough to show certain properties of bulk solids, but are also small enough to maintain quantized electronic states. These quantized effects exist due to the sizes of the distances between electron-hole pairs that exist in the excited states of the quantum dot. For many semiconductor nanocrystals, this distance is approximately 10 nm, resulting in a particle-in-a-box situation for excited quantum dot energy levels. The electronic properties of quantum dots have been extensively studied, and many substantial applications for these structures are currently being investigated and developed [1].

While many studies have focused on the individual properties of quantum dots, relatively few have investigated the electronic states of quantum dot arrays. In research performed by Woggon *et al*, arrays of quantum dots were examined to see what would become of the electronic states as the quantum dots were grouped closer together [2]. His results showed that as the spacing between quantum dots was decreased, a transition from isolated to delocalized electron states was observed. The electronic band structure of the quantum dots diminished and eventually disappeared into a continuum of energy states. These results demonstrated the similarities that could exist between semiconductors and quantum dot arrays. Our study investigates the same phenomenon found by Woggon using methods of optical absorption and electroabsorption.

Chapter 2

The Experiment

2.1 Quantum Dot Synthesis

The synthesis of the quantum dots was done following the work of Woggon [3]. The quantum dots in this case were CdSe nanocrystals. They were formed by combining 10 mL of a 2×10^{-2} M solution of cadmium acetate in pyridine with a solution of selenourea that had been dissolved into 1 mL of pyridine. The combined solution had a Cd:Se ratio of 2:1. In the original experiment, the solutions were combined at 80 °C under nitrogen flow, and a stir bar was also used to aid the combination of the CdSe nanocrystals. My initial CdSe synthesis was done in the same manner as the synthesis done by Woggon. Dry pyridine was used, and the solutions were combined at 80 °C under nitrogen flow. The CdSe solution was then studied using absorption. The resulting absorption graph is displayed in Figure 2.1. Due to the difficulty of performing the synthesis with minimum exposure to air and water, we worked on recreating the synthesis in air using wet pyridine. We varied the temperature at which the solutions combined, and we compared their respective absorption spectra to see which temperature would yield a solution with the most similar absorption spectrum to the first. After several attempts, we found that combining the cadmium acetate and selenourea solutions at 70 °C in air yielded the most similar absorption spectrum (Figure 2.1), and we used this method for creating CdSe throughout the rest of our research.

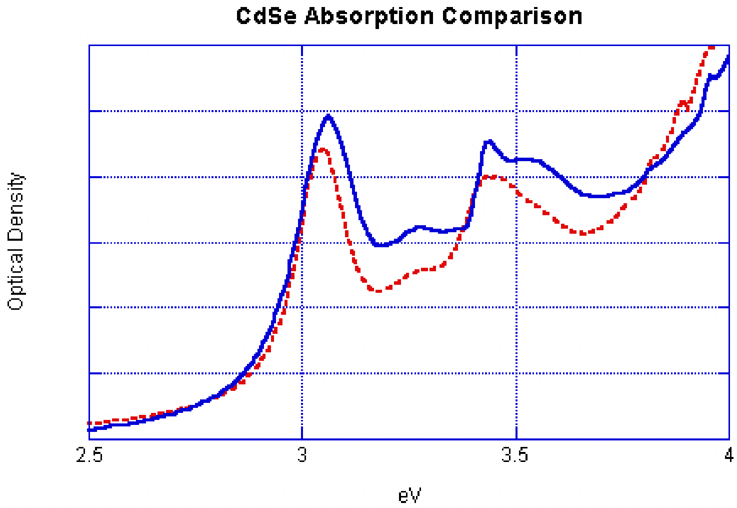

Figure 2.1 Absorption spectra of CdSe nanocrystals in pyridine solution. The dashed curve corresponds to the synthesis done following Woggon. The other corresponds to the synthesis performed at 70 °C without precautions.

Once the CdSe solution was made, the nanocrystals were then separated from the pyridine. This was done by adding an agent to the solution that would attach itself to the nanocrystals. The nanocrystals would gain a semi-protective monolayer and would immediately fall out of solution. The purpose of the capping layer was to stabilize the nanocrystals to keep them from combining into crystals that were too large. In the synthesis done by Woggon, 1/2 mL of thioglycerol was used for this purpose. Once the CdSe had precipitated out of solution, it was centrifuged, washed twice with methanol and then redispersed into a fresh pyridine solution via ultrasonic treatment. When we began this stage of the synthesis, no thioglycerol was immediately available, so we ventured to find a substitute for it. We experimented with thioglycol, thioglycerine, thiophenol, and thioglycolic acid. We found that thioglycol caused the CdSe to precipitate, but when it came to redistributing the nanocrystals back into solution, the crystals destabilized. This was observed through a darkening of the solution as the crystals underwent ultrasonic treatment. The nanocrystals would combine into larger crystals with more electron energy states that were capable of absorbing light in the visible spectrum. Thioglycerine produced similar results when used as the capping agent. We tried several different concentrations of solution and different methods of CdSe creation to see if the nanocrystals would stabilize, but the results didn't improve significantly. The ultimate objective was to create a final nanocrystal solution that could be dried to make films ideal for absorption and electroabsorption studies. We tried using thiophenol, which stabilized the nanocrystals sufficiently to keep them from combining during sonication, but the films made using thiophenol-capped nanocrystals had a low optical density. The films were incapable of absorbing enough light to generate meaningful data during absorption experiments. Last of all, thioglycolic acid created a precipitate too thick to be properly centrifuged. Finding a substitute for thioglycerol proved to be difficult.

In time, thioglycerol was obtained for the experiment. Surprisingly, the thioglycerol-capped CdSe also ran into destabilization problems if it was left in ultrasonic treatment for too long. Only by stopping the ultrasonic treatment as soon as the nanocrystals went into solution (the solution became clear before darkening significantly) could the nanocrystal destabilization be avoided. Once the nanocrystals were back in solution, a few drops of the solution were placed on a glass slide and allowed to dry. The resulting films were often not transparent and were not well suited for optical experiments. Various drying methods and environments were explored, but none consistently produced clear films. The films were dried covered and uncovered at various temperatures ranging approximately from 16 °C to 40 °C. After numerous test runs, clear films were obtained by chance, and these were preserved for use in absorption experiments.

In order to create films with greater CdSe nanocrystal spacing, PMMA was added to the final CdSe solution. The films containing PMMA dried clear much more readily than those that did not. PMMA was used for its transparent qualities, which meant that its influence during optical experiments was minimal. The approximate ratio by mass used for PMMA:CdSe was roughly 2:1, and several concentrations of solution were experimented with to find which was most useful for creating clear films. It was found that 19 mg of CdSe with approximately 38 mg of PMMA dissolved into 1 mL of pyridine produced good films. This concentration was achieved by first dissolving the PMMA into 1/2 mL of pyridine and then adding it to 1/2 mL of CdSe solution. In this way, heat could be used to dissolve the PMMA in the absence of the nanocrystals. These concentrations deviated from those used by Woggon, but it was necessary for producing CdSe films that could successfully be used in absorption and electroabsorption experiments.

2.2 Electrode Preparation

Electrodes were used to place an electric field across the dried CdSe films for the electroabsorption experiment. Each electrode was made from a 1 cm diameter sapphire disk (approx 2 mm thick) with a patterned layer of chromium put on one side. The chromium pattern was divided into two separate conducting sections that were used to maintain a voltage difference across the disk. The spacing between the chromium digits was 127 microns, and the ends were rounded to help reduce high-voltage induced arcing (See Figure 2.2). A CdSe sample was simply placed over the chromium pattern and the two sections of chromium were put in contact with an oscillating voltage source, thus creating a strong electric field across the sample. The electrode allowed light to pass through due to the good transparency of the sapphire and the gaps in the chromium pattern. In this way, the absorption of the CdSe sample could be studied while an electric field was put across the sample.

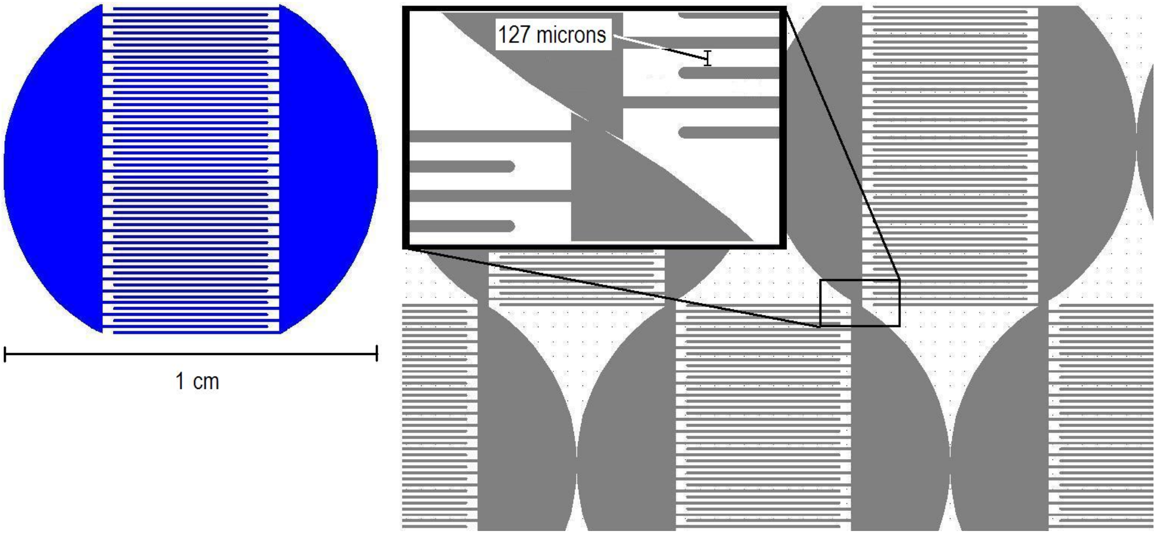

Figure 2.2 Images of the electrode pattern. On the left is the complete pattern for one electrode with the dark areas representing chromium. On the right is a small portion of the mask with a close up view of the electrode design.

Multiple steps were involved in creating the electrodes for the electroabsorption experiment. First, the sapphire disks had to be cleaned in order to keep foreign substances from impeding chromium adhesion. The disks were washed with hexane and acetone and scrubbed with a non-metallic abrasive pad. They were then baked in an oven at nearly 1000 °C for 30 minutes in order to remove any organic residues. After the disks were cleaned, chromium was evaporated onto the disks in a vacuum chamber. The chamber was put under a vacuum of about 6 μTorr and a filament containing chromium deposits was heated using electrical current until the chromium evaporated. The sapphire disks, which were mounted on a metal plate and suspended in another part of the chamber, eventually gathered a layer of chromium approximately 1 angstrom thick. The initial evaporation run was not successful because the wax that was used to mount the disks melted and covered the disks as the chromium was evaporating. Cleaning the disks a second time was difficult since there was no chemical available that could effectively remove the chromium from the disks. A solution of hydrochloric acid in water (one part water to three parts HCl) was used to remove the chromium, but the process was slow and chromium traces remained on some disks after the cleaning. The second run was more successful since much less wax was used to mount the disks for the evaporation. After the second deposition, the disks were washed with acetone to clean off the wax that remained. During the washing, many disks lost large portions of their chromium because of surface impurities. Only a few disks were clean enough to keep their chromium well attached. These disks were the ones used to make the final electrodes.

Once the chromium was deposited, negative photolithographic procedures were used to etch the electrode pattern into the chromium. The first step to performing the photolithography was creating a mask specifically designed to etch the needed pattern. The mask outline first had to be made using a special drawing program. Once the outline picture was ready, a computer-controlled machine loaded the outline and made the actual mask. A portion of the drawing can be seen in Figure 2.2. The completed mask consisted of a square glass plate (4 inches to a side) with multiple electrode patterns placed throughout, which allowed several disks to be exposed at once. Each electrode pattern on the mask was a negative image of the final product. Thus, the mask allowed light to reach the places on the chromium where the metal was intended to stay. Once the mask was ready, negative photoresist was placed onto the chromium using spinners that applied the photoresist in an even layer. As soon as the photoresist was spun, the disks had to be baked on a hot plate at 80 °C for one minute. After that, the disks were ready to be exposed. The disks and mask were loaded into a machine that was used to align the mask correctly over the disks as well as expose the photoresist. After the exposure was done, the disks had to be baked for another minute at 80 °C. A developer solution was used next to remove the unexposed photoresist, and this left the chromium exposed in the areas where the chromium was meant to be removed. All that remained was to place the disks into a chromium etchant solution for about a minute, and the electrode pattern was complete. The leftover photoresist could be removed using acetone without affecting the chromium underneath. This whole process was repeated numerous times until enough electrodes were successfully made for use in the experiment.

2.3 Electroabsorption

2.3.1 Setup

Electroabsorption tests were run on the CdSe nanocrystal films once the electrodes were ready. A few drops of CdSe solution were placed directly onto the electrode and allowed to dry. The strength of the electric fields applied to the sample by the electrodes ranged from 6×10^4 to 8.5×10^4 V/cm. A 150 W Xe lamp was used as the light source. The light was sent through a spectrometer, through the sample, and then to a detector using mirrors to focus the light both through the sample and onto the detector. A power supply coupled with a signal generator provided the oscillating voltage source for the electrode, which was run at 3900 Hz. This frequency resonated best with the power supply and therefore allowed for the largest voltage output. A 300 Hz light chopper was also used to modulate the light source to run T-scans for the experiment. The T-scan was simply a transmission spectrum of the substrate and the sample combined. Both the voltage frequency and the light chopper, when used with the lock-in amplifier, were means devised to reduce noise in the experiment. A diagram of the setup can be seen in Figure 2.3.

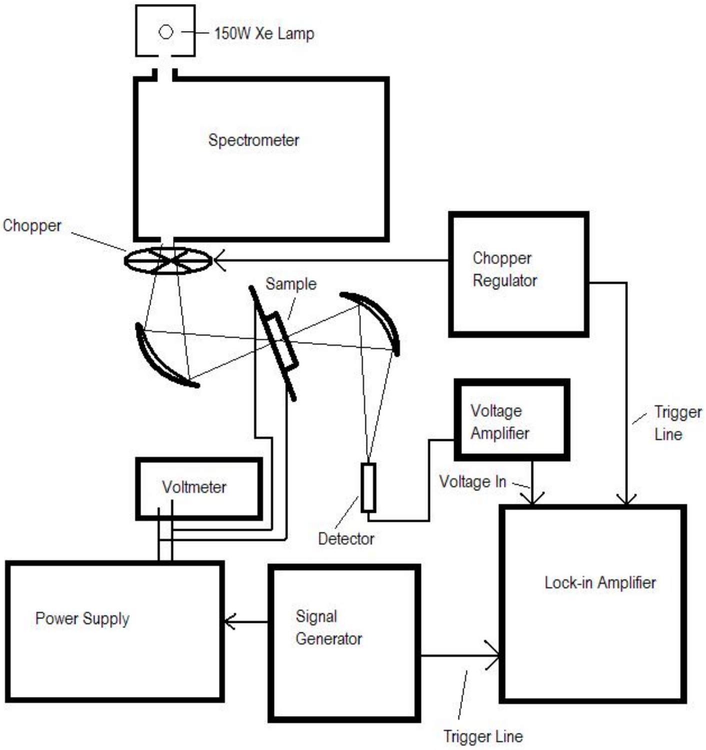

Figure 2.3 Shown here are the main components of the electroabsorption experiment.

2.3.2 Running the Experiment

In order to do the electroabsorption experiment, we would first run a T-scan on the sample. It would show me the wavelengths of light that would give the strongest signals. Thus we could scale the electroabsorption data by dividing the electroabsorption results by the T-scan results. This would make sure that the magnitude differences between the electroabsorption peaks were not simply due to more light passing through the sample. Any time we ran a T-scan, we would have to make two adjustments to the setup. First, we had to make sure that the phase on the lock-in amplifier was set correctly to obtain the maximum signal output. This phase adjustment was necessary any time we used the lock-in amplifier. Second, we would find the wavelength where the signal was the greatest (within the range of wavelengths we was interested in studying), and then we would adjust the slit width until we could get the greatest signal on the lock-in amplifier without overloading the input signal. The lock-in amplifier was only capable of reading signals up to 1 V in amplitude. This adjustment allowed us to use the most amount of light possible without passing the limits of the equipment.

The primary work in obtaining good electroabsorption data had to do with trying to control the signal to noise ratio while not overloading the detector and lock-in amplifier. Four things could be modified to find the best signal: the slit width of the spectrometer, the sample thickness, the electric field strength, and the lock-in amplifier time constant. First, the slit width could be changed to allow more light to pass through the sample. Naturally, the more light that was passed through the sample, the larger the difference would be between the absorption with and without the electric field. This would therefore increase the signal. On the other hand, more noise was usually introduced with more light. Also, if too much light reached the detector, it would cause the lock-in amplifier to overload. Thus, increasing the slit width had its limitations. Second, thicker samples would also yield larger differences between the absorption with and without the electric field. The obvious downside was that if the sample became too thick, not enough light would reach the detector to give a significant signal. Third, the signal size could be increased by raising the oscillating electric field strength. The only problem was that if the voltage put across the electrode became too great, the electric field would break down and arcing would occur across the electrode. Lastly, if all else failed, I could always increase the time constant on the lock-in amplifier. This would increase the time over which the signal was averaged before giving a reading, which in turn smoothed out some of the noise.

2.3.3 Getting Results

After running numerous electroabsorption scans, we were able to find certain things that helped us to improve our results. For example, we found that by completely covering the electrode with the CdSe film, we could increase the voltage across the electrode to approximately 650 V without running into problems with arcing. Increasing the voltage created more dramatic shifts in the energy states of the CdSe nanocrystals, and this was much more easily picked up by the lock-in amplifier. Another aid we found was that of putting a plate between the sample and the detector. The plate would not block the main light path, but it would rather keep extra scattered light from going directly from the sample to the detector, thus reducing the signal noise.

Apart from these adjustments to the experiment, our data gathering methods were aided by the lock-in amplifier. In principle, applying an electric field to the CdSe films should cause the nanocrystal energy levels, or equivalently the absorption peaks, to shift. Most often these shifts are very small and can only be seen by taking the difference between the the two absorption spectra (one with and one without the electric field). The was the approach used by Woggon. He simply ran two absorption spectra, one with and one without the electric field, and then took their difference. Our experiment, however, registered the shifts in energy levels in a more direct manner. While using a fixed-frequency oscillating voltage source, the lock-in amplifier is sensitive to only the signals that came in at a specified frequency, thus helping to reduce the noise in the experiment.

Chapter 3

Results

3.1 Analysis

The various results obtained from the experiment indicate that the electronic levels of the quantum dot arrays become meshed as the spacing between the quantum dots is decreased. Figure 3.1 shows the initial absorption data collected from two different CdSe films. One film contains PMMA to increase the nanocrystal spacing. The graphs show the absorption spectra of the two samples, and it is clearly seen that the sample containing sparse quantum dots (the one with PMMA) shows absorption peaks corresponding to energy bands and gaps in the CdSe energy levels. The second graph, however, shows much less defined absorption peaks. The band gap qualities of the sparse quantum dot array is lost once the quantum dots become closely packed together.

A part of this trend can also be seen in the electroabsorption graphs. Figure 3.2 contains two graphs depicting the places of greatest shifting in energy states for the CdSe film containing PMMA during electroabsorption. The peaks in the electroabsorption graph correspond to places where the absorption levels shifted the most under

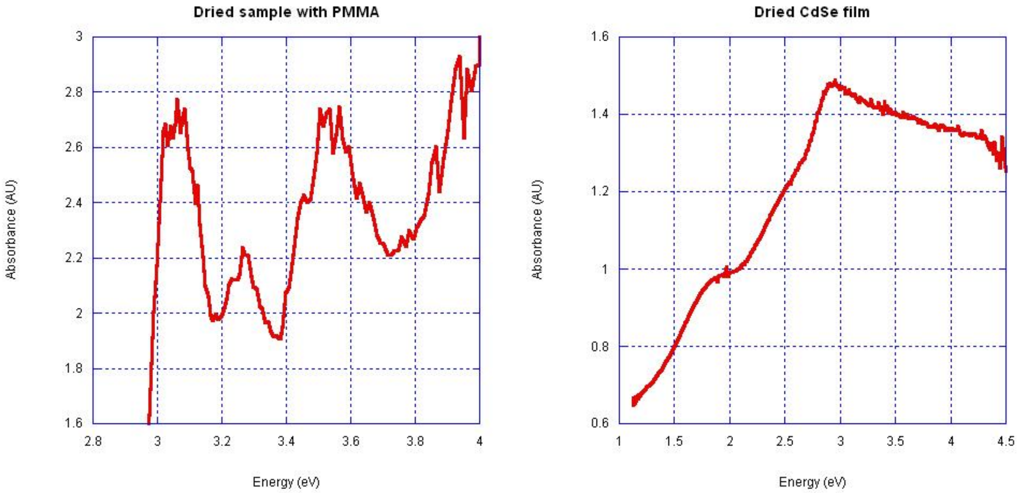

Figure 3.1 Absorption graphs for films of CdSe quantum dots with and without PMMA added.

the influence of an electric field. Greater shifts often correspond to energies at which the slope on the absorption graph is the greatest. Troughs in the electroabsorption graph often correspond to negative slopes on the absorption graphs (this changes, however, depending on the direction of the shift). Therefore, when interpreting the peaks and troughs in the electroabsorption data, it is assumed that they are related to the band gap structure of the substance being examined. Due to time constraints, reliable electroabsorption data for close-packed CdSe films was not obtained, but the data for the CdSe sample with PMMA does indicate the presence of absorption peaks.

For extra demonstration, a graph of the derivative of an absorption curve of a CdSe film with PMMA is shown in Figure 3.3. This graph shows similarities to the electroabsorption graph in Figure 3.2. This goes to further show the relationship between absorption slopes and electroabsorption shifts.

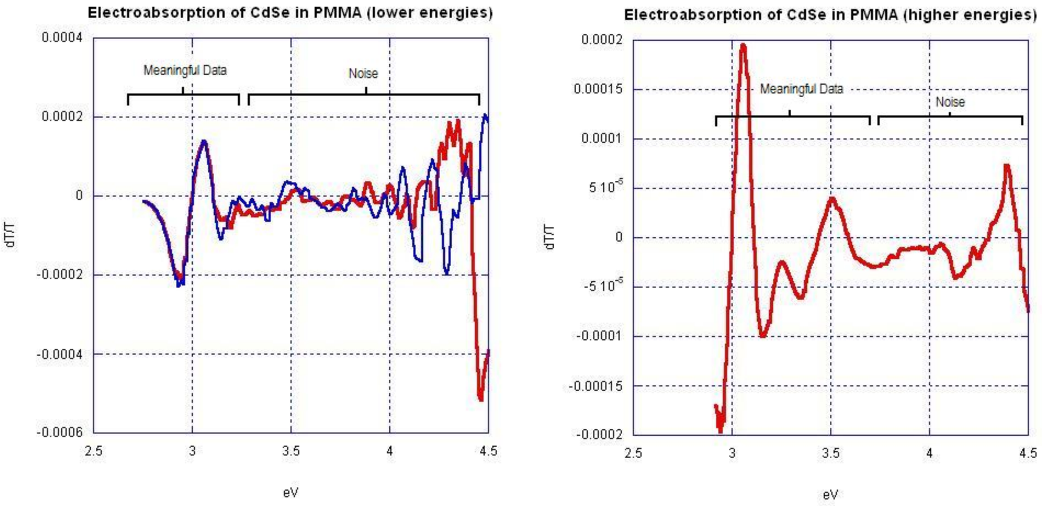

Figure 3.2 Electroabsorption graphs for a single CdSe film with PMMA. Each graph contains different portions of the same electroabsorption curve for the CdSe film. Different experimental settings were used to obtain the data in each graph. The graph on the left completely shows the first lower energy level shifting while the graph on the right shows the shifting for energy levels up to 3.7 eV. The y axis scale shows the change in transmission (due to the electric fields) divided by the overall transmission spectra.

3.2 Conclusion

The data from the absorption graphs helps demonstrate that the spacing between quantum dots in dot arrays is directly related to the structure of the electronic energy levels of the material. The absorption data suggests that the gaps in the energy levels of the quantum dot arrays become narrow and eventually disappear as the quantum dot spacing is reduced. The electron states become delocalized around multiple quantum dots, and the particle-in-a-box situation is removed. The electroabsorption data also shows the existence of peaks in quantum dot energy transitions for sparse arrays, but insufficient electroabsorption data was gathered for the close-packed CdSe samples to show how the CdSe energy levels changed with decreased nanocrystal spacing. Future work with electroabsorption may produce useful data for further

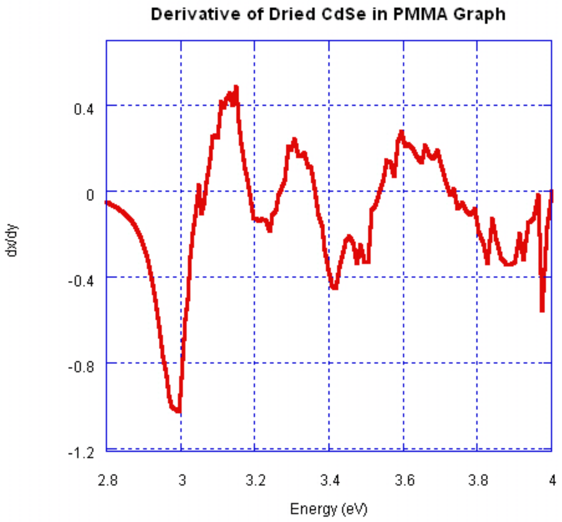

Figure 3.3 Derivative of the absorption graph of the CdSe film with PMMA.

understanding the energy levels of close-packed CdSe nanocrystals.

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